

660.51

Synthetic Organic Chemicals

PUBLISHED BY THE
EASTMAN KODAK COMPANY, ROCHESTER, NEW YORK

VOL. IV

PUBLISHED OCTOBER, 1930

No. 1

Removal of Water from Organic Compounds

THE presence of small amounts of water in the materials being used for an organic preparation sometimes influences the result very markedly. Claisen condensations, Grignard reactions, and many others will not take place if moisture is present in the reacting materials. The physical constants of an absolutely anhydrous product often differ materially from those obtained on an insufficiently dried sample. An exaggerated example of this is the apparent high boiling point of benzene which has been noted after it has been dried for years, and about which much controversy has occurred. It is possible to prevent the waste of expensive anhydrides, acid chlorides, and other compounds that react with water, by drying the materials to be used with a cheaper dehydrating agent before starting the reaction.

Fused anhydrous calcium chloride is one of the most used dehydrating agents since it is quite inexpensive and may be obtained in a convenient granular form. It is not as vigorous as some of the other reagents but is often used for preliminary dehydrations. The granular form is particularly suitable for drying gases since it can be packed in a tower and the moist gas admitted at the bottom. Most of the water is thus absorbed in the lower end of the tower, and as the solid particles liquefy they run down the side in droplets and do not obstruct the passage of

the gas. The upper part of the column remains practically dry so that the gas is subjected to the most active material as it leaves. Trimethylamine is easily freed of water in this manner. Calcium chloride is not suitable for use with some of the acidic compounds with which it forms salts nor for dehydrating alcohols on account of its tendency to form addition compounds.

The alcohols can be dehydrated with potassium carbonate or calcium oxide. Aluminum oxide is now available commercially and is said to be an efficient dehydrator for alcohols. Water can be removed from methyl alcohol without any special treatment other than careful fractional distillation. Ethyl alcohol is more difficult to dehydrate. It not only forms a constant boiling mixture with water but also reacts with concentrated sulfuric acid to form ethyl-sulfuric acid, and with anhydrous sodium hydroxide to give the ethylate. The laboratory preparation of anhydrous ethyl alcohol is usually accomplished by refluxing and distilling over calcium oxide. This treatment is not so necessary now as formerly since anhydrous ethyl alcohol is being manufactured on a large scale. The commercial process depends on the formation of a low-boiling "azeotropic" mixture of alcohol-water-benzene or alcohol-water-ethyl acetate. This can be distilled off at a temperature below the boiling point of the alcohol itself, taking

all of the water with it. The remaining benzene is removed by simple fractionation. The separation is more effective if the distillation is carried out at 10 atmospheres instead of at ordinary pressure.

The formation of constant boiling mixtures also aids materially in many laboratory separations. "Wet" benzene can be purified by simple distillation, the first fraction containing all of the benzene-water mixture. Distillation is continued until the condensate ceases to come over cloudy. The anhydrous benzene boils at a higher temperature than the mixture, so remains in the flask. Water can be removed from toluene, tetrachloroethane, and carbon tetrachloride in a similar manner.

Carbon tetrachloride is especially useful in separating water from hydroscopic or very soluble materials. Malonic acid is a product which holds on to water tenaciously but is easily dehydrated by distilling with carbon tetrachloride. By means of a separatory tube the distillation can be carried on continuously, the water being discharged while the dry solvent returns to the flask containing the malonic acid. In order to remove the ammonium chloride which is formed as an impurity in the preparation of trimethylamine hydrochloride, it is necessary to dry the material thoroughly. This can also be easily done by the carbon tetrachloride method.

In contrast to distillation, crystallization can sometimes be used to separate water from a compound. Repeated crystallization of acetic acid through freezing and pouring off the liquid gives a product of 99.9% purity. Tertiary butyl alcohol can be freed from water in a similar manner. Laboratory centrifuges are often a help in drying other solids, since they remove the bulk of the water more rapidly and completely than ordinary filtration, thus reducing the time required for subsequent drying.

The use of the vacuum desiccator with sulfuric acid as the drying agent is still one of the most convenient ways of absorbing water, especially from small amounts of material. It has almost no substitute for drying extremely hydroscopic materials or products that must not be exposed to the light. Sulfuric acid has the additional advantage that it will remove ethyl and iso-propyl alcohols. Desiccators are also useful in removing small amounts of ligroin that may remain from the purification of substances like diphenylhydrazine. In this case the sulfuric acid is replaced by paraffin which is a surprisingly effective absorbent for the hydrocarbons.

In spite of its effectiveness as a dehydrating agent, sodium is used only in small amounts, principally for removing the last traces of water. Careless handling of sodium can easily cause violent explosions, so for this reason other agents are used whenever possible. Sodium is particularly helpful in the removal of water from piperidine and other amines after they have been given a preliminary treatment with powdered anhydrous sodium hydroxide. Alloys of sodium and potassium can be made which will be liquids at ordinary temperatures. They are more effective than metallic sodium since the mobile alloy continually presents a fresh surface to the liquid.

The necessity for having dry materials in the preparation of Grignard reagents is well known. When the ether or alkyl halide contains moisture, the reaction is very difficult to start. If a small amount of methylmagnesium bromide or one of the other Grignard compounds is kept on hand, a few cubic centimeters can be added to the mixture. This immediately reacts with the water present, thus allowing the principal reaction to proceed. With the compound suggested, methane would be formed, and being an easily removable gas, would not contaminate the final product.

An Improved Manometer for the Organic Laboratory

MERCURY manometers are indispensable in the organic preparation laboratory, yet they require a great deal of attention and careful use to keep them accurate at all times.

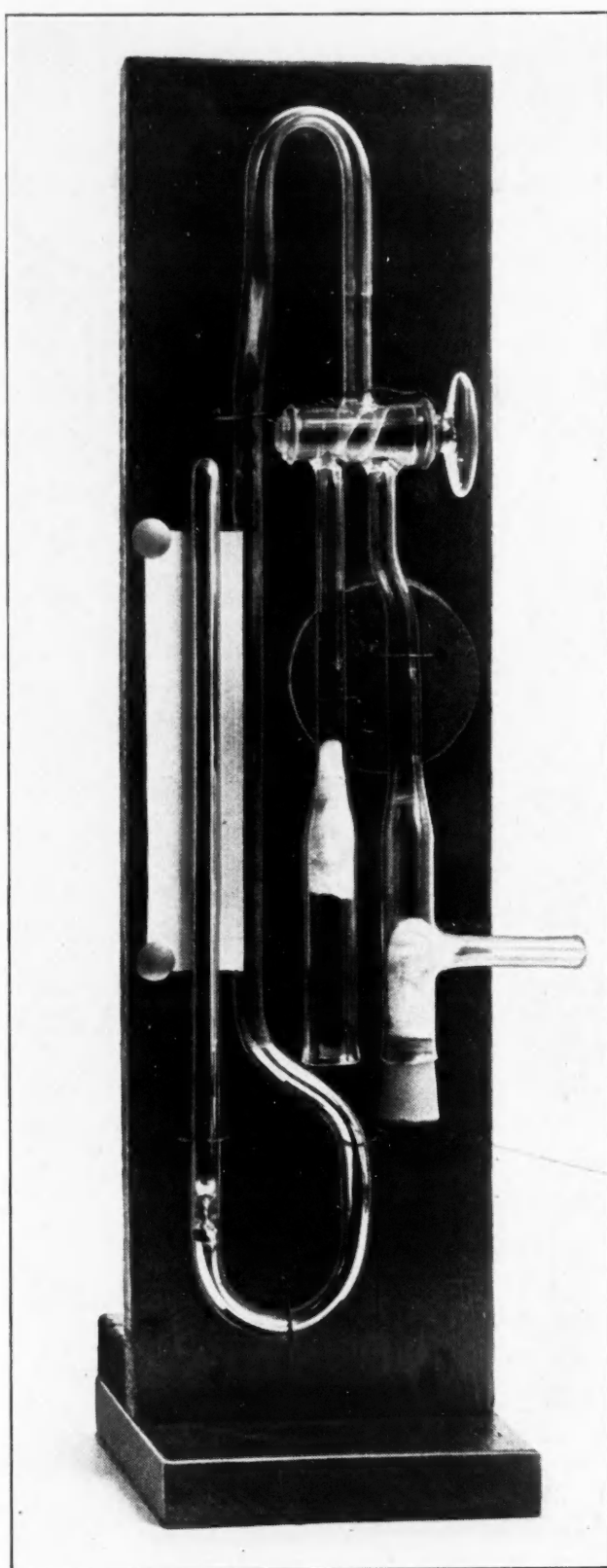
Where they are used continually in a vacuum distillation set-up, the mercury becomes contaminated from the vapor of the distillate and rapidly forms a scum, which collects on the side of the manometer tubing. This interferes with the free movement of the meniscus, and before long makes readings impossible. It is practically impossible to clean the tubing after it is bent into shape, so as soon as the gauge becomes unfit for use it must be discarded and replaced by a new one.

We have found that by adding an extra inlet tube to the manometer the ordinary trouble is almost entirely prevented. With this second tube and a two-way stopcock, the column can be released by admitting outside air instead of by drawing the vapor of the distillate over into contact with the mer-

cury. Where a large number of manometers are used, the increased life means an appreciable saving.

Two other changes in construction may be noted in the accompanying illustration, although they are not entirely new. The sharp bend at the bottom of the U-tube is rounded out in order that a strong bend of even thickness may be made by the glass blower without the employment of unusual skill. The apparatus is protected from breaking through sudden opening of the vacuum line, by a capillary constriction in the left column. This can be formed without weakening the tubing, by pushing it together very slightly while turning the glass in a hot flame until the side walls thicken sufficiently to form a capillary of the desired diameter.

We have had a few of these manometers in use in our organic laboratory for some time, and find them so satisfactory that we are replacing all of the older models with this type.



Eastman Organic Chemicals as Analytical Reagents

XVI. REAGENTS FOR MAGNESIUM (continued)

DIMETHYLAMINE

Herz and Drucker: *Z. Anor. Chem.*
26, 347 (1901)

Magnesium is precipitated as the hydroxide in the presence of salts of the alkali metals by a cold aqueous Dimethylamine solution. After standing a while, most of the liquid is decanted and the residue filtered, using wash water containing a small amount of Dimethylamine. After drying, the precipitate is ignited and weighed as magnesium oxide.

8-HYDROXYQUINOLINE

Hahn and Vieweg: *Z. Anal. Chem.*
71, 122 (1927)

A 5% alcoholic solution of 8-Hydroxyquinoline makes a convenient reagent for precipitating magnesium from the alkali metals. The dilute test solution, containing about 100 mg. of the metal per 100 cc., is warmed and treated with an excess of the reagent. The solution is made slightly ammoniacal and allowed to stand on the water bath for a time. After cooling, the precipitate is filtered, and washed with dilute ammonia and finally with water. It is kept in an oven at 100° to 120° until dry, then heated to 140–160° so that a constant weight is obtained. The dry precipitate contains 7.78% magnesium.

OLEIC ACID

Yoe: *Photometric Chemical Analysis*
(1928)

The formation of a pale yellow colloidal suspension of magnesium oleate is the basis of this method. A sample containing about 0.1 mg. is treated with a 10% ammonium chloride solution, then with a reagent consisting of an alcoholic solution of Oleic Acid and potassium hydroxide. After diluting and

allowing to stand, the color is compared with that of a sample in which the magnesium content is known. Calcium behaves similarly, so it must be removed before the test.

New Eastman Organic Chemicals

During the summer months the following chemicals were added to our stock, which now includes over 2,700 items. Those marked with an asterisk are made in our own laboratories.

- *2-Aceto-1-naphthol
- Acetyl Benzoin
- *o-Bromodiphenyl
- *p-Bromodiphenyl Ether
- *p-Cresyl Ethyl Thioether
- pseudo-Cumene (Technical)
- *Cyclohexyl Adipate
- *4,4'-Dibromodiphenyl
- *4,4'-Dibromodiphenyl Ether
- *Diethylene Glycol Monobenzyl Ether
- *1,3-Dihydroxy-4-chlorobenzene
- 4,5-Diphenylglyoxalone
- *β-Ethoxyethyl Lactate
- *Ethyl α-Chloroacetoacetate
- *Ethylene Glycol Diformate
- *Ethylene Phenylsulfide
- Ethyl Ethyl-iso-amylmalonate
- Ethyl Ethylmalonate
- *β-Hydroxyethyl Formate
- *Itaconic Acid
- *3-Methyl-5-pyrazolone
- *2,2,3,4,4-Pentachloro-1-keto-1,2,3,4-tetrahydronaphthalene
- *Piperine
- Potassium Periodate (Practical)
- Sodium Periodate (Practical)
- *m-Thiocresol
- *p-Thiocresol